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STRUCTURE OF ZIRCONIA NANOPARTICLES USED FOR PILLARING OF CLAY

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ABSTRACT

SAXS and EXAFS were applied to study genesis of polynuclear zirconium hydroxyspecies in pillaring solutions as dependent upon the zirconium concentration, addition of alkaline-earth chlorides and aging. After the montmorillonite clay pillaring, the structure of zirconium nanopillars was characterized by applying X-ray structural analysis, UV-Vis, FTIRS of adsorbed CO and nitrogen adsorption isotherms. Main pillaring species appear to be nanorods comprised of several Zr_4 tetramers. Basic structural features of the tetramers are preserved in zirconia nanoparticles fixed between alumosilicate layers in pillared clays. In calcined samples, those nanoparticles contain only bridging hydroxyls and/or oxygen anions responsible for bonding within pillars and between pillars and clay sheets.

INTRODUCTION

Clays pillared by nanosize zirconia particles (Zr PILC) are promising supports and catalysts for different petrochemical processes [1-2] and selective catalytic reduction of NO_x by hydrocarbons in excess oxygen [3]. Their performance strongly depends upon the size, shape and structure of nanosized zirconia pillars propping the alumosilicate layers, which are in turn determined by the properties of zirconium hydroxy polycations in pillaring solutions. The majority of published data on pillared clays synthesis mainly concerns studies of the effects of preparation procedures and properties of starting clays, while little attention has been paid to the shape and structure of pillaring species formed in solutions.

In this work, to cover this gap, SAXS and EXAFS were applied for investigation of the early stages of zirconium salts (zirconyl chloride and acetate, concentration 0.1-0.3 M) hydrolysis during aging at temperatures in the range from 25 to 80 °C. In addition, the effect of the alkaline-earth cations (Ca, Sr and Ba) on this process was considered as well. The X-ray structural analysis, UV-Vis and FTIRS of adsorbed CO were used to further characterize the zirconia nanoparticles in the calcined pillared montmorillonite clays.

EXPERIMENTAL

Zr-containing solutions (Zr concentration 0.1-0.3 M) were prepared from recrystallized $ZrOCl_2$ 8 H_2O and zirconium acetate (Aldrich 41 380-1, solution in diluted acetic acid). Those were modified by adding chlorides of Ca, Sr and Ba with variation of the Zr:Me ratio in the range of 3.3-9.0. Next series of solutions were prepared and studied:

I.   Zirconium salt or its mechanical mixture with Ca, Sr or Ba chlorides was dissolved in the distilled water immediately before spectra recording (Fresh).

II.   1.0 M solutions of zirconium chloride containing alkaline earth chlorides (0.1-0.3 M) were diluted and kept at a room temperature for 8 days (Aged RT).

III. Solutions of series I were aged at 55 °C for 16 h.

IV.   Solutions of series II were aged at 80 °C for 3 h.

Zirconia-pillared clays were synthesized using a Ca – or Na-montmorillonite clay from the Kazakhstan deposit containing 66 wt. % SiO_2 and 25 wt. % Al_2O_3 following earlier described procedures [4] and pillaring solutions of IV series.

Solutions were studied using the X-ray Small-Angle Scattering (SAXS, a KPM-1 camera with Cu K_α radiation) in the range of 2θ angles 7'-4° and EXAFS (the spectra were acquired at the EXAFS station of the Siberian Center of Synchrotron Radiation, Novosibirsk) using procedures and data analysis described in details previously [5].

The size distribution of zirconium polynuclear species in solution $D_n(r)$, where r is a characteristic size of a particles, (i.e., a sphere radius for spherical particles) was derived by using the Equation (1)

$$I(q) = \int D_n(r)\, m^2(r)\, i_o(qr)\, dr \tag{1}$$

Here, $I(q)$ is the measured intensity of scattering, $q = 4\pi \sin\theta/\lambda$ - amplitude of the wavevector, with $\lambda = 1.54$ Å being the wavelength of the X-ray beam, $m(r)$ –the difference between the dielectric constants of the scattering particle and surrounding media, $i_o(qr) = [3(\sin qr - qr \cos qr)/q^3 r^3]^2$ – the intensity of scattering on a given spherical particle with a radius r [6]. The SAXS data analysis using a relation $\log I \sim q^2 R_g^2/3$, where R_g is a gyration radius [6] was attempted as well.

The X-ray phase analysis of the initial and pillared clays was carried out using a HZG-4 (C,B) diffractometer (Cu K_α radiation and a flat monochromator) in the range of 2θ angles equal to 1-60°. To obtain the curves of the electronic density radial distribution, Mo K_α radiation and a bent graphite monochromator were applied for measurements in the 2θ range 3-140°.

Adsorption characteristics were measured on a Micromeritics ASAP-2400 installation by N_2 adsorption at 77 K.

UV-Vis spectra were recorded using a Shimadzu 8300 spectrometer equipped with a diffuse scattering DRS 8000 cell. Spectra were recorded in the 10000-60000 cm^{-1} range with 4 cm^{-1} resolution, the number of scans being equal to 50. Samples were loaded into the vacuum cells equipped with CaF_2 windows. To decrease the mirror reflection, a sample layer was inclined for 20-25% with respect to the horizontal plane.

The surface properties were probed by the IR spectroscopy of adsorbed CO test molecule (FTIRS, a Fourier-transform IFS 113V Bruker spectrometer).

RESULTS

Solutions

Fig. 1 shows typical SAXS dependencies for solutions containing 0.1 M of zirconium salts. Aging conditions very strongly affect the intensity of scattering in the range of small q values, while the alkaline earth cations and the nature of starting salts were mainly reflected in the high q part of curves. These curves contain several inflection points thus suggesting that there is a size distribution of zirconium polynuclear species. As a result, direct estimation of the gyration radius from these curves as in [6] appears to be ambiguous. The analysis of the

particle size distribution by applying the integral Equation (1) revealed that in fresh diluted solutions of pure zirconium salts polynuclear zirconium hydroxocomplexes are mainly represented by species with typical sizes in the range of 15-30 Å. They are comprised of several Zr_4 tetramers stacked into nanorods. The EXAFS data confirm preservation of the parent Zr_4 structure in those species characterized by the next typical distances and coordination numbers (CN): Zr-O - 2.21 Å (CN 7), Zr-Zr - 3.34 Å (CN 0.8), Zr-Zr - 3.67 Å (CN 1) and Zr-Zr - 4.91 Å (CN 0.8). It implies a weak interaction (mainly through the hydrogen bonds) between stacked tetramers in oligomerized zirconium hydroxycomplexes.
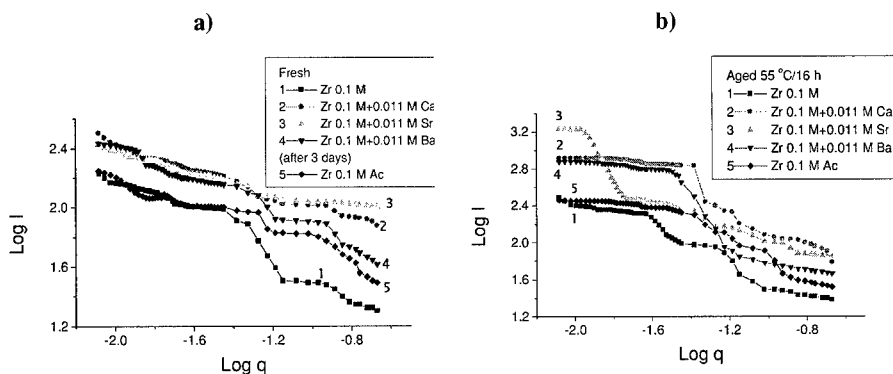

Fig. 1. SAXS intensity for fresh (a) and aged at 55 °C/16 h (b) solutions containing zirconium salts.

In aged solutions especially in those aged at 80 °C, the tetrameric units appear to be bound stronger, which is reflected in pronounced distortion of their structure. In this case, only two distances: Zr-O - 2.19 Å (CN 7) and Zr-Zr - 3.52 Å (CN 0.8) are revealed in the EXAFS spectra. These features can be tentatively explained by a structure of nanorods in which consecutively stacked Zr_4 units are rotated by 45 degrees relative to each other to ensure their connection by bridging OH groups formed by condensation of terminal OH groups situated at the vertexes of tetramers. The existence of sheet-like structures where disordered stacking of coplanar tetramers occurs could not be excluded as well, though formation of the latter species seems to be less probable.

In pure solutions of zirconium salts, a part of zirconium hydroxocomplexes is aggregated into large (typical diameters in the range of 60-200 Å) colloidal particles. The addition of alkaline-earth cations into solutions helps to partly suppress formation of those particles not affecting appreciably the structure of nanorods, only slightly decreasing Zr-O and Zr-Zr coordination numbers. Some increase of nanorods mean sizes (up to 45 Å) was observed as well. As alkaline-earth cations are found to be completely removed from the pillared clays at the washing stage, it suggests that in solutions, they are located at the external surface of nanorods being coordinated by terminal hydroxyls or water molecules chemically bound with Zr cations of tetramers. Such an interaction explains a higher distortion of the tetramer structure leading to decrease of EXAFS coordination numbers (in aged solutions, in the

presence of alkaline-earth cations, Zr-O CN are in the range of 6.6-6.3, while Zr-Zr CN are in the range of 0.7-0.3). The lowest coordination numbers were found for Sr-containing solutions, and the highest -for solutions with added calcium chloride. Some variation in the structure of polynuclear species in the presence of different alkaline earth cations as suggested by these results can be tentatively explained by the difference in the hydration sphere of the latter cations in water solutions [7]. Thus, for Ca the nearest sphere is comprised of regular octahedron, for Ba it is elongated octahedron, while for Sr it is a square antiprism. It can be speculated that Sr cations are included within the polynuclear species affecting the mode of their polymerization and condensation at aging.

Clay structure and texture

In the initial clay washed by the diluted HCl solution with the pH value 2.2 equal to that in pillaring solutions and then calcined at 400 °C, the basal (001) spacing was found to be ~ 11 Å (9.6 Å being the reference value for completely dehydrated parent montmorillonite). The mean particle size in the (001) direction was around 40 Å. After pillaring, washing and calcination at 400 °C, for all samples studied here and containing ~ 20 wt.% of zirconia, the basal spacing was increased up to ~ 18 Å, while the particle size remains rather constant (~ 30 Å), suggesting that pillaring has not caused the clay exfoliation. These results imply that for all samples studied here, the mean gallery height is around 7 Å. This value corresponds to the normal orientation of tetrameric units with respect to the host layers.

In all zirconia- pillared clays studied here, any reflections which could be assigned to separate zirconia-containing phases were not observed. It means that for predominant part of pillars, their typical sizes within the basal plane are less than 25-30 Å, and that in the basal direction is less than 10 Å. The differential radial distribution curve obtained by subtracting the initial clay data from those of pillared clays was found to contain maxima at 2–2.4; 3.6; 4–4.2; 4.5–4.8; 5.6–5.9 Å, thus proving incorporation of the tetrameric units containing species into the clay structure (Fig. 2).
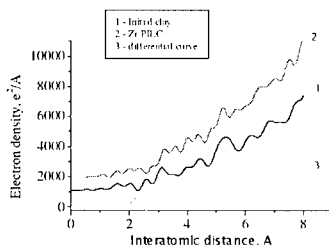

Fig. 2. Electron density radial distribution curves for the initial clay (1), Zr PILC (2) and differential (2-1) curve (3).

The negative peaks of the electron density in the differential curve show variation in the structure of a clay due to pillars incorporation. The interlayer distance between the tetrahedral SiO_4 layers in the alumosilicate sheets is increased up to 2.8 Å. Similarly, the distance between octahedrally coordinated cations (Me=Al, Mg) to the oxygen in the nearest tetrahedron is increased from 3.1 to 3.3 Å. These variations can be caused by strains generated by zirconia

pillars situated between the alumosilicate layers. The incorporation of a big cation (first of all, Zr) into the vacant octahedral positions could not be excluded as well.

As follows from the results of UV-Vis (Fig. 3), for Zr PILC the characteristic absorption corresponding to the anion-cation charge transfer is shifted to higher wavenumbers as compared with that for the bulk analog -highly dispersed cubic zirconia stabilized by 2 mol. % of CaO [8]. This feature can be explained by a lower O-Zr coordination number in nanosized pillars (maximum 2 for bridging oxygen anions or hydroxyls) as compared with the bulk zirconia lattice (each oxygen is surrounded by 4 Zr cations). As a result, the Zr-O bond in nanoparticles possesses a higher ionicity which is reflected in a higher energy of the charge transfer band. Decreased intensity of those bands in Zr PILCs can be related to a high disordering of the nanoparticle structure as revealed by EXAFS [8].
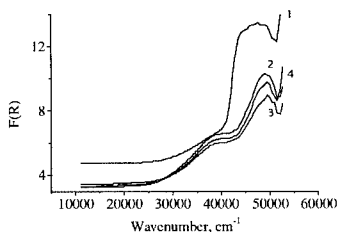

Fig. 3. UV-Vis spectra of bulk cubic zirconia stabilized by calcium (1) and zirconia-pillared clays prepared by using pillaring solutions containing Ca (2), Sr (3) and Ba (4) cations.

According to analysis of the nitrogen adsorption isotherms by using the geometric model of pillared interlayer materials [9], the specific surface area of a free space within the pillared clay galleries is in the range of 350-400 m^2/g. A mean diameter of pillars approximated by discs was estimated to be in the range of 15-20 Å, which agrees rather good both with the predominant sizes of pillaring species in solution and the upper limit of the size of zirconia nanoparticles as determined by XRD (vide supra).

FTIRS data of adsorbed CO and hydroxyl groups (not shown here for brevity) indicate that on the surface of zirconia pillared clays evacuated at 400 °C, the number of coordinatively unsaturated Zr cations is much lower as compared with that for bulk highly dispersed zirconia samples [8]. Moreover, in the hydroxyls stretching regions, only bands at ~ 3650-3700 cm^{-1} corresponding to bridging hydroxyls are present. It implies that the surface of zirconium nanoparticles is covered by bridging hydroxyls binding either Zr cations or Zr cations and cations in the alumosilicate layers.

CONCLUSIONS

The structural features of zirconium polynuclear hydroxyspecies in pillaring solutions (degree of polymerization and internal arrangement) were shown to depend upon the presence of electrolytes (alkaline-earth chlorides) and aging conditions. Fixation of those species between clay sheets causes rearrangement of both the alumosilicate layers and pillars. Low Zr-O coordination numbers in zirconia nanoparticles are reflected in the high-frequency shift of the Zr-O charge transfer band indicating increased ionicity of this bond.

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